A Review on Current trends in Heavy Metal Removal from Water Between 2000-2021

ABSTRACT

Recent fiscal growth has necessitated diverse industrial processes to meet the growing demands around the world. Toxic chemicals such as micro-pollutants, personal care products, pesticides contaminate the effluents of these industries and find their way into the environment leaving dangerous levels of heavy metals in the aquatic ecosystem. These heavy metals such as arsenic, chromium, lead, mercury, cadmium and nickel bio-accumulate and are very harmful to humans. Several water treatment methods were reviewed from 111 published articles covering a period between 2000-2021 on the progress of Heavy Metal removal from waste water including the use of low cost agro based activated carbon and Bentonite clay as part of "green and sustainable chemistry".

KEYWORDS: Heavy Metals, Adsorption, Chemical Precipitation, Membrane Filtration, Pillared Clay, Electrodialysis, Photocatalysis, Water treatment.

1. INTRODUCTION

Heavy metals are posing concern in aquatic ecosystems because of their persistence, bioaccumulation and environmental toxicity, PBT [1], [2], [3]. Due to the industrial revolution, large quantity of industrial wastes are been discharged into sewage networks giving rise to increasing value of heavy metal contents in wastewater [4]. Some of the heavy metals include lead (Pb), arsenic (As), mercury (Hg), chromium (Cr) specially hexavalent chromium, nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se), vanadium (V) found in oils and grease, pesticides, etc are very harmful, toxic and poisonous even in ppb (parts per billion) range [5].

2. HEAVY METALS IN WATER

2.1 Sources of Heavy Metals

Heavy metals enter the environment by natural activities of weathering of earth crust and rocks and anthropogenic activities with include mining and various industrial discharges. A study of surface water bodies by [6] as shown in Table 1 indicates the major heavy metal sources differentiated across the five continents.

Table 1: Sources of Heavy Metals across the Continents

S/N	Continent	Major Source of Heavy Metals	Contribution Percentage
1	**Africa**	Fertilizer and pesticide use; rock weathering	56.7
2	**Asia**	Mining and manufacturing ;rock weathering	97.1
3	**Europe**	Mining and manufacturing; rock weathering	56.2
4	**North America**	Mining and manufacturing ; fertilizer and pesticide use	90.4
5	**South America**	Waste discharge; Mining and manufacturing, fertilizer and pesticide use ;rock weathering	93.5

2.2. Definition, Toxicity and Effects

Heavy metals are naturally occurring elements that have a high atomic weight and a density greater than that of water. Heavy metals are an important class of pollutants which can produce considerable harm to the environment when they are above certain concentrations [7]. The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human [8]. Some of the metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential nutrients that are required for various biochemical and physiological functions with specific permissible limits as prescribed by World Health Organization (WHO) . The most toxic to humans and animals are Lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As). The adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include neurotoxic and carcinogenic actions .Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration, it is well-known that chronic exposure to heavy metals and metalloids at relatively low levels can cause adverse effects [9], [10].

The maximum allowable limits of heavy metals in water established by Nigerian Standard for Drinking Water Quality (NSDWQ), World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) are shown in Tables 2 and 3

Table 2: Maximum Permissible limit of Heavy Metals for Drinking Water

Parameter	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Se	Zn

WHO(2006)	0.1-0.2	0.01	0.3	0.05	2	0.3	0.1	0.02	0.01	0.01	4
NSDWQ(2007)	0.2	0.01	0.1	0.05	1	0.3	0.2	0.02	0.01	-	3
USEPA(2009)	0.05-0.2	0.01	2	0.1	1.3	0.3	0.05	-	0.015	0.05	5

Units: mg/L

Table 3: NSDWQ Permissible limits of Heavy Metals Concentrations of Normal Drinking Water

Parameter	NSDWQ standard (mg/L)	Health Impacts
Aluminum	0.2	Potential Neuro-degenerative disorders
Arsenic (As)	0.01	Cancer
Barium	0.1	Hypertension
Cadmium (Cd)	0.003	Toxic to the Kidney
Chromium (Cr)	0.05	Cancer
Copper (Cu)	1	Gastrointestinal disorder
Iron (Fe)	0.3	None
Lead (Pb)	0.01	Cancer, interference with Vitamin D metabolism, affect mental development in infants, toxic to the central and peripheral nervous systems
Manganese(Mn)	0.2	Neurological disorder
Mercury (Hg)	0.001	Affects the kidney and central nervous system
Nickel (Ni)	0.02	Possible carcinogenic
Zinc (Zn)	3	None

Source: [11]

Arsenic: Arsenic is a metalloid and is rarely found as a free element in the natural environment, but more commonly as a component of sulphur-containing ores in which it occurs as metal arsenides [12]. Arsenic is one of the most important heavy metals of concern as it has been identified that exposure to arsenic through drinking water over a long period of time is the cause of multiple adverse health effects including diabetes; peripheral neuropathy; cardiovascular diseases; and skin, lung, bladder and kidney cancers [13]. Inorganic arsenic is considered carcinogenic and is related mainly to lung, kidney, bladder, and skin disorders [8]. Following a thorough review and in order to maximize health risk reduction, the USEPA in 2001 decided to reduce the drinking water maximum contaminant limit (MCL) to 0.010 mg/L, which is now the same as the WHO guidelines [14]. In Nigeria investigations into Arsenic contamination of

groundwater [15], [16], [17] and surface water [18] have been found to be above the maximum contaminant limit as specified by WHO.

Lead: Lead as one of the heavy metals of importance, though it is a naturally occurring substance, but anthropogenic activities like burning of fossil fuels and mining have contributed to the discharge of high levels of it in the environment. It is an important raw material for many products such the production of lead-acid batteries and other metallic products. In humans, the kidney is most affected by lead [19]. Lead toxicity also targeted towards the memory and learning processes of the brain and can be mediated through three processes. Lead can impair learning and memory in the brain [20].

In Nigeria, most industries discharge their effluents into water bodies particularly rivers and streams and as such whatever hazardous elements from the effluents contaminate the water [21], [22]. A Case of lead poisoning in recent times is the 2010 lead poisoning in Bagega Village of Zamfara State, Nigeria in which 17,000 people were affected and 500 casualties were recorded due to mining activities that led to contamination of domestic water source [23], [24].

Cadmium: Cadmium is a heavy metal of considerable toxicity with destructive impact on most organ systems [25] chronic exposure to the metal can lead to kidney disorders, anemia, emphysema, anosmia (loss of sense and smell), cardiovascular diseases, renal problems, and hypertension [26]. Itai itai disease appears to be a Cadmium -related disease, which is very painful and causes the wastage and embrittlement of bones [27].

A summary of the toxicity of heavy metals commonly associated with environmental contamination are given in Tables 4, 5 and 6. They are divided into essential, non essential and mixed essential heavy metals.

Table 4: Essential Heavy Metals for different Organisms

Heavy Metal	Organism	Essentiality	Toxicity
Zinc (Zn)	Plant	Yes	Chlorosis (Fe-deficiency-induced), stunted plant growth and reduced yield
	Animals	-	Diarrhea, anorexia, jaundice, kidney and abomasums damage, arthritis and weight loss
	Humans	Yes	Diarrhea, nausea, vomiting, epigastric pain, lethargy, anemia, neutropenia, impaired immune function and decreased HDL cholesterol.

	Plant	Yes	Leaf bronzing, roots with black coating and reduced plant growth. Common in flooded rice.
Iron (Fe)	Animals	Yes	Anorexia, diarrhea, metabolic acidosis, reduced body growth rate and death.
	Humans	Yes	Vomiting, diarrhea, metabolic acidosis and increased risk of atherosclerosis and Alzheimer's disease
	Plant	Yes	General chlorosis, necrotic leaf spots and stunted plant growth.
Manganese(Mn)	Animals	Yes	Anemia, gastrointestinal lesions and growth retardation
	Humans	Yes	Psychiatric disturbance and neurodegenerative disorder, including Parkinson's disease.

Source: [28], [29]

Table 5: Non Essential Heavy Metals for different Organisms

Heavy Metal	Organism	Essentiality	Toxicity
	Plant	No	Chlorosis, root system darkening, stunted plant growth and increased oxidative stress
Lead (Pb)	Animals	No	Appetite loss, diarrhea, anemia and body weight loss
	Humans	No	Neurological problems (from headache topsychosis) and kidney damage
	Plant	No	Hypertrophic root, retarded plant growth and increased oxidative stress.
Mercury (Hg)	Animals	No	Vomiting, bloody diarrhea and necrosis of the alimentary mucosa
	Humans	No	Neurological disturbances, kidney damage and decreased fertility
	Plant	No	Increased oxidative stress and reduced plant growth
Arsenic (Ar)	Animals	No	Blindness and reduced weight gain
	Humans	No	Increased cancer risk.

Source: [28], [29]

Table 6: Mixed Essential Heavy Metals for different Organisms

Heavy Metal	Organism	Essentiality	Toxicity
Chromium (Cr)	Plant	No	Increased oxidative stress and reduced plant growth. Cr(VI) is more toxic than Cr(III).
	Animals	No	No effect recognize as of the time of this research
	Humans	Yes	Allergy and increased cancer risk. Cr(VI) is more toxic than Cr(III) or Cr(V).
	Plant	Yes	Increased oxidative stress, retarded germination, stunted root growth, chlorosis, inhibited plant growth and reduced yield.
Nickel (Ni)	Animals	No	No effect recognize as of the time of this research
	Humans	No	Skin allergies, lung fibrosis, kidney and cardiovascular system damage and stimulation of neoplastic transformation
Manganese(Mn)	Animals	Yes	Anemia, gastrointestinal lesions and growth retardation
	Humans	Yes	Psychiatric disturbance and neurodegenerative disorder, including Parkinson's disease
	Plant	No	Chlorosis, wilted and dried leaves, reduced plant growth and plant premature death.
Selenium (Se)	Animals	Yes	Impaired vision, anemia, loss of hair, ataxia, stiffness of joints, paralysis, atrophy of heart and death
	Humans	Yes	Hypochromic anemia, damaged nails and hair loss.

Source: [28], [29]

3. CONVENTIONAL REMOVAL PROCESS

Water and wastewater treatment processes are chosen mainly based on the initial quality of the water, on the parameters established by regulations and on the proposed use [30].

3.1 Chemical Precipitation

Precipitation is the process by which dissolved metals are made insoluble, usually as metal hydroxides, metal sulfide, and metal carbonate [31].This is a conventional method of removing heavy metals from

water and is usually divided into pretreatment, precipitation and post treatment phases. The solid formed is known as the precipitate and the liquid residue is called the supernatant.

Precipitation agents (ligands) work by increasing the pH of the wastewater usually by an alkaline agent which reduces the concentration of the metals in solution causing them to precipitate. These are then removed by sedimentation and other filtration processes as shown in Figure 1. Effectiveness of the chemical precipitation is affected by the type and concentration of metal ions present in the solution, precipitation reagent used, reaction conditions, and presence of other compounds that can inhibit the reaction [32]. Though pH plays a vital role in the process of chemical precipitation, a number of environmental factors can influence mineral precipitation in a wastewater including the amount of mineral phase present in the wastewater and wastewater temperature [33]. The presence of chelating compounds which form complexes can also inhibit metal precipitation. Choice of ligands utilized depends on cost and efficacy of treatment [31]. Common ligands used are sulfides, carbonates and hydroxides and are shown in Table 7.

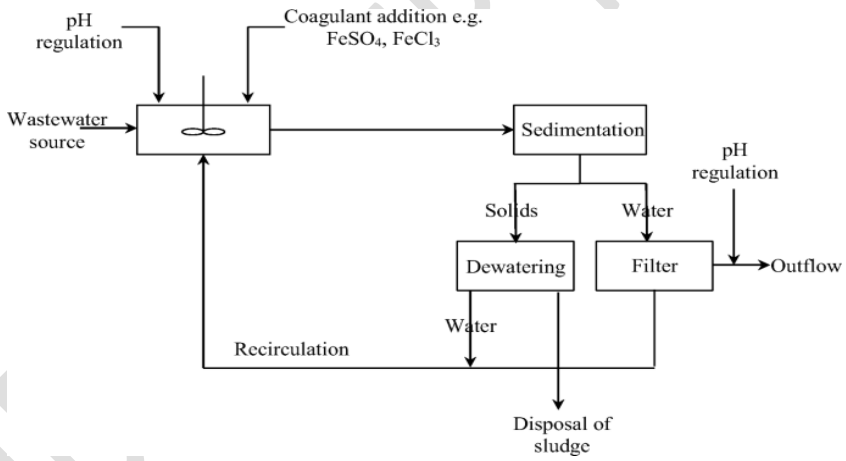


Figure 1 Schematic of Chemical Precipitation Process [32]

[34] studied the removal of Arsenic from waste water using hydrated lime and ferric chloride and achieved 98.9% reduction from initial concentration of the contaminant. [35] achieved a 98.4% removal of Nickel in water purification.

[36] studied the treatment of heavy metal wastewater with magnesium hydroxy carbonate to reduce the concentrations of Cr^{3+} and Fe^{3+} in wastewater. The result showed the removal efficiencies of heavy metals were above 99.9% with concentrations of Cr^{3+} and Fe^{3+} at 0.05 and 1.12 mg/L, respectively, which conformed to the limit of discharge set by China.

[37] and [38] investigated the removal of Cr(VI) from industrial waste water using a combination of Ca(OH)2 + NaOH and found that the maximum removal of 98.2% and 100% were achieved respectively.

Though chemical precipitation has been found as an effective method for heavy metal decontamination of water, a major disadvantage of the process is the formation of a large quantity of metal precipitate which requires further treatment and disposal.

Table 7: Common ligands used for Chemical Precipitation

Ligand	Metals	Comments
Hydroxide (sodium hydroxide (caustic soda) and calcium hydroxide (lime))	Cadmium, chromium, nickel, lead	Calcium hydroxide not to be used in wastewater with high sulfates to avoid scaling
Carbonates	Lead, cadmium, nickel	Produces large precipitates
Sulphides (sodium and calcium)	Arsenic, copper, mercury, lead	Odour due to the production of hydrogen sulfide

4. ADSORPTION

The adsorption process is an efficient and effective method for the removal of a wide variety of toxic pollutants from raw water. Activated carbon has been globally recognized as the oldest, most widely used, and popular adsorbent in the water and wastewater treatment industries [39], [40] The adsorption mechanism is defined by the physicochemical properties of adsorbent and heavy metals and operating conditions which include temperature, adsorbent amount, pH value, adsorption time, and initial concentration of metal ions [41].The choice of suitable absorbent varies depending on its application. Cost, Kinetics, compatibility, selectivity, capacity and regenerability are important characteristics that affect the choice of adsorbents. It has been noted through various researches that most good adsorbents have optimal ratings in at least 2 of these attributes.

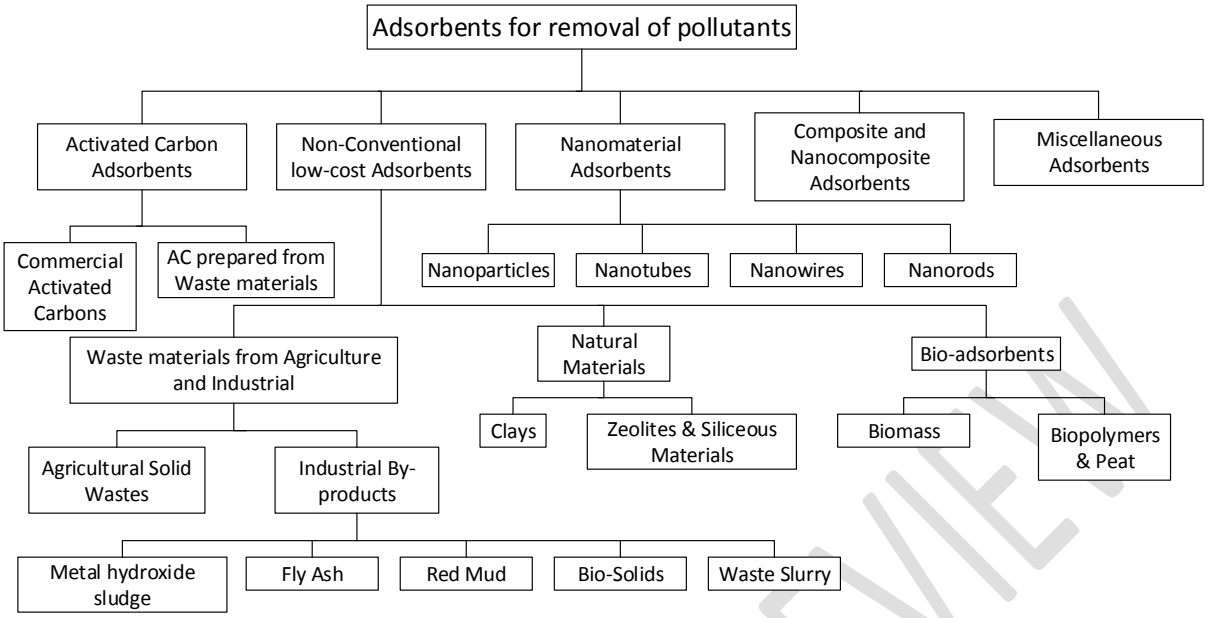


Figure 2 Classification of Adsorbents for Heavy Metal Removal [42]

4.1. Low Cost Agro Activated Carbon

Activated carbon is distinguished from elemental carbon by the absence of both impurities and an oxidized surface [43]. The raw material is carbonized to obtain the char or carbonaceous material, which is then activated to yield the highly porous product which has high degree of porosity and an extended internal surface area [44]. It has been noted that typical values of carbon content and ash content of a good activated carbon should range from 60 – 98% and 2-6.5% respectively [45]. High carbon content value is desired to achieve high surface area because as the carbon content of the activated carbon increases, the surface area also increases [46]. Other characteristics of activated carbon include Iodine Value, Moisture content, Density, Particle size distribution and Porosity.

Comparative analysis of commercial activated carbon and activated carbon from some agricultural residue was carried out by [47]. The percentage composition of Iodine value obtained from imported activated carbon (12.143 %), coconut husk (60.1 %), maize husk (38.1 %), palm kernel shell (24.286 %) and coconut shell (63.571 %) and the percentage surface area of imported activated carbon (42 %), coconut shell (21 %), coconut husk (24.1 %), maize husk (33.1 %) and palm kernel shell (37 %) The results of Iodine value and surface area of the activated carbons produced and imported activated carbon were investigated and revealed the efficacy of the produced activated carbon as a great substitute for the commercial grade carbon.

[44] investigated the adsorption capacity of activated bamboo by chemical and physic-chemical activation methods and results characterized in terms of surface area, porosity, bulk density, carbon yield and ash content. It showed that the Physic-chemical activation has the highest surface areas (4839m^2/g and 5415 m^2/g) at 400^{o}C and 500^{o}C. It also further stated that the activating chemical need not be washed to avoid generating more wastewater during production.

A study by [48] on characterization of local mango (Magnifera indica) seeds as good precursor for activated carbon yielded an activated carbon from Chur-kpev and Dausha (local varieties of mango) with carbon contents of 93.7% and 92.8%, respectively.

[49] investigated the use of Nigerian bamboo as an alternative to commercial activated carbon for the simultaneous adsorption of six heavy metal ions(Cd^{2+},Ni^{2+},Pb^{2+},Cr^{3+},Cu^{2+} and Zn^{2+}) in refinery waste waters.

The equilibrium and kinetics of adsorptive capacity of H_3PO^{4-} and NH_4Cl^- treated Afzelia africana (A. africana) wood sawdust was studied by [50]. Results of saw dust characterization in Table 8 show saw dust as viable activated carbon

Table 8: Characterization of Saw Dust Activated Carbon

Parameters SDA SDS	H_3PO^{4-} TSD	NH_4Cl^- TSD
BET surface area (m^2/g)	315.873	187.839
Total pore volume (cm^3)	0.731	0.704
Bulk density (g/cm^3)	0.206	0.553
Ash content (%)	3.010	2.113
Moisture content(%)	5.840	5.795

Source: [50]

Animal Bones have been used effectively for the production of activated carbon. [43] characterized bone char from cow, donkey, chicken and horse at carbonization temperature of 400^{o}C for 2.5 hours. The percentage weight loss where 63%, 58%, 54% and 62% for cow, donkey, chicken and horse bones respectively. The percentage of carbon yield of cow, donkey, chicken and horse bones upon acid activation are in increasing order of cow (48.92%) > horse (48.64%) > donkey (46.34%) > chicken (44.80%) bones and horse (37.03%) > cow (36.21) > donkey (34.96%) > chicken (30.18%) upon heat

activation. It was also noted that the chicken bone had the least ash content of 12.84%, 11.05% and 15.84% for acid, heat and non-activated samples respectively. Table 9 shows a summary of adsorption of heavy metals using low cost agro based adsorbents.

Table 9: Adsorption of Heavy Metals using Low cost Agro Based Activated Carbon

Adsorbent	Metal	Initial Conc (mg/L)	Initial pH	Contact time(mins)	Adsorbent dose(g)	Removal efficiency(%)	Reference
Bamboo	Cd(II)	50	5	60	5	87.81	[51]
Bamboo	Pb(II)	50	11	150	5	96.45	[51]
Bone char	Cd(II)	10	5	60	1	99.4	[52]
Bone char	Pb(II)	10	5	60	1	99.89	[52]
Cassava peels	Pb(II)	5.3	8	120	12	73	[53]
Cassava peels	Cu(II)	4	8	120	12	79	[53]
Coconut husk	Pb(II)	0.005	2	80	1	100	[54]
Coconut husk	Fe(II)	16.6	2	80	1	84.1	[54]
Coconut husk	Cu(II)	43.5	2	80	1	78.16	[54]
Coconut husk	Zn(II)	17.4	2	80	1	34.77	[54]
Corn cob	Pb(II)	100	N/A	120	2.5	95	[55]
G/nut shell	Fe(II)	5.9	N/A	120	1	100	[56]
G/nut shell	Cr(III)	0.6	N/A	120	1	98	[56]
G/nut shell	Cu(II)	3.4	N/A	120	1	70	[56]
G/nut shell	Mg(II)	15	N/A	120	1	9	[56]
G/nut husk	Mn(II)	N/A	6	80	50	61.62	[57]
G/nut husk	Zn(II)	N/A	3	60	20	100	[57]
G/nut husk	Pb(II)	N/A	6	80	60	99.93	[57]
Palm Kernel	Cd(II)	1.82	N/A	60	0.5	99.24	[58]
Palm Kernel	Ni(II)	3.24	N/A	60	0.5	95.34	[58]
Palm Kernel	Pb(II)	2.62	N/A	90	0.5	97.75	[58]
Palm Kernel	Cu(II)	1.52	N/A	60	0.5	96.71	[58]

Periwinkle	Cr(III)	100	6	120	1.2	94.13	[59]
Periwinkle	Zn(II)	100	6	120	1.2	87.91	[59]
Plantain peel	Zn(II)	50	5	100	1.5	91.17	[60]
Plantain peel	Cu(II)	50	9	140	1.5	93.83	[60]

*G/nut= groundnut. N/A= not available

4.2 Clay (Bentonite)

Bentonite is used as an adsorbent for removal of metal ions because of its cation exchange capacity, larger surface area and adsorptive capacity for different organic and inorganic ions [61]. Modification of Bentonite can be achieved by various methods which include thermal activation [62], acid activation [63], pillaring [64], [65], modification using surfactants [66], [67].

[61] studied the adsorption of selected heavy metals(Cr(VI),Hg(II),Pb(II)and Cd(II)) on a silk-Bentonite composite(0.05g) and observed a percentage removal efficiency of >85 of heavy metal ions. It was noted that adsorption percentage decreased by increasing temperature as increase in available thermal energy increases mobility of adsorbate causing desorption. Therefore optimum adsorption was achieved at lower temperature.

The effects of pH and temperature on lead removal were investigated by [62] using calcined Bentonite (500^{o}C). Results indicated removal efficiency increased from 13.4 to 91.74% for Pb^{2+} by increasing the solution pH from 2.0 to 5.0. However, increasing temperature from 20^{o}C to 60^{o}C impacted negatively on adsorption capacity from 92 to 38 mg/g of Pb^{2+}. This is the resultant effect of desorption produced by an increase in the available thermal energy which alter the adsorption–desorption equilibrium [62]

Modification of Bentonite clay by acid activation was investigated by [68] with results of maximum adsorption capacities of 10.52 mg g^{-1} and 5.56 mg g^{-1} obtained for acid-modified and unmodified Bentonite clay samples.

Pillared Clay: this is achieved by changing the nature which modifies and creates a composite with different pore-sizes. Clay is subjected to dehydration to present pore spaces for adsorption but excessive dehydration causes the collapse of the inter-layers. Pillaring of clay ensures that the clay maintains its porosity during the hydration or dehydration process. This increases the high surface area and porosity for adsorption purposes. This porosity combined with the properties of both pillar and host are very important for certain adsorption applications [69]. [64] modified natural Bentonite clay to pillared clay by the use of mixed oxide pillars of aluminium and zirconium. Figure 3 schematic of pillared clay and

Figure 4 shows the SEM of natural Bentonite and the pillared Bentonite clay samples with ultrasonication times of 5, 10 and 20 minutes.

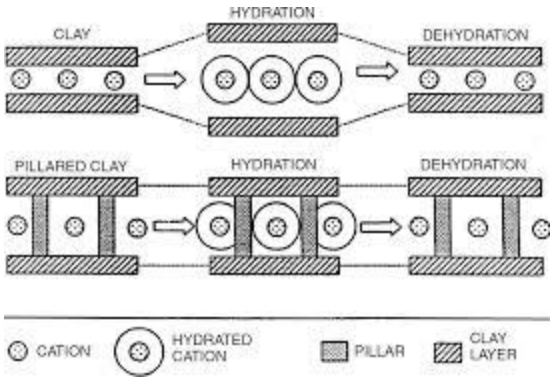
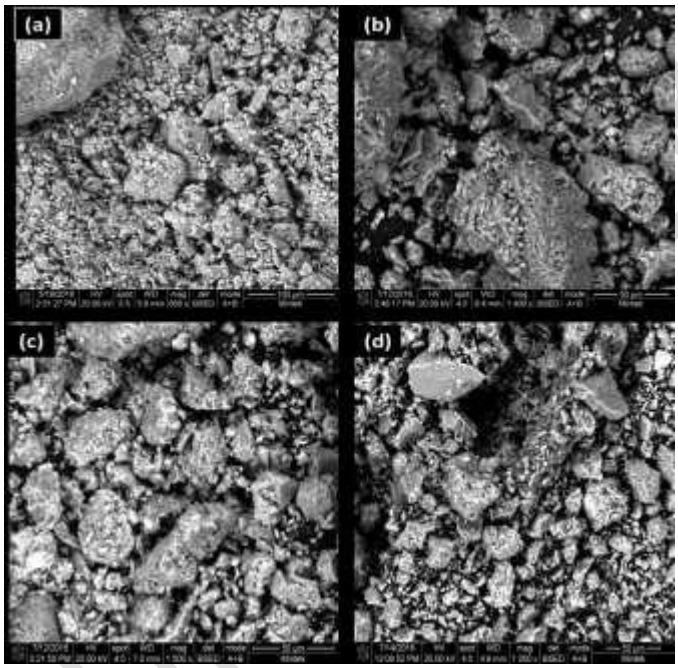


Figure 3: Schematic of pillared clay [69]



(a) Natural Bentonite clay, (b) Al/Zr-PILC (3:1, 5 min), (b) Al/Zr-PILC (3:1, 10 min), (b) Al/Zr-PILC (3:1, 20 min).

Figure 4: SEM imaging of Unmodified and Pillared Bentonite clay [64]

Results indicated that the resultant Zr/Al-pillared Bentonite exhibited higher BET surface area and pore volumes compared to unmodified Bentonite material. It was also noted that increase in ultrasound

treatment resulted in a decrease in surface area and pore volumes. Optimum results are obtained with short ultrasonic treatment times (10 minutes).

A summary of results using Bentonite as adsorbent is shown in Table 10.

Table 10: Adsorption capacity of clay

Clay	Metal	Conc (mg/L)	pH	Time (Mins)	Dosage (g)	Adsorption capacity (mg/g)	%	References
Unmodified	Pb(II)	50	6	120	1	26.3	N/A	[70]
Silk-Bentonite composite	Cd(II)	10	5	60	0.05	11.35	92	[61]
Silk-Bentonite composite	Pb(II)	10	5	60	0.05	11.1	93	[61]
Silk-Bentonite composite	Hg(II)	10	5	60	0.05	10.5	85	[61]
Silk-Bentonite composite	Cr(II)	10	5	60	0.05	10.2	88	[61]
Unmodified	Cd(II)	10	5	120	2	N/A	94.34	[71]
Unmodified	Cu(II)	10	6	120	2	N/A	99.23	[71]
Calcined	Pb(II)	50	5	140	0.1	92	90.23	[62]
Unmodified	Pb(II)	2000	N/A	720	1	83.02	N/A	[63]
Unmodified	Cd(II)	2000	N/A	720	1	48.20	N/A	[63]
Unmodified	Cu(II)	2000	N/A	720	1	30.99	N/A	[63]
Acid Modified	Pb(II)	2000	N/A	12(hours)	1	92.85	N/A	[63]
Acid Modified	Cd(II)	2000	N/A	720	1	57.88	N/A	[63]
Acid Modified	Cu(II)	2000	N/A	720	1	36.68	N/A	[63]

5 .MEMBRANE FILTRATION

A membrane is a selective layer with a porous or non-porous structure that is used to make contact between two homogeneous phases to remove the different size of pollutants [72]. It is essentially a barrier, which separates two phases and restricts transport of various chemicals in a selective manner [73]. It is a thin layer of semi-permeable material that separates substances when a driving force (chemical or electrical potential) is applied across it.

Membrane filtration involves the separation of particles from a solution by means of a membrane. This process (Figure 5) separates the influent into two distinctive effluents; the flow that passes through the membrane (permeate) and the constituents that are rejected/stopped by the membrane. This has made the process of immense importance in the separation of organic and inorganic constituents (which include heavy metals) from contaminated water. Membrane technologies have moved into the area of treating secondary or tertiary municipal wastewater and oil field related water [73]. Parameters that affect the efficiency of membrane filtration are materials in use, membrane pore size and composition [72].Classification of type of membrane filtration used depends on the size of particle to be removed from solution. Microfiltration, Ultrafiltration, Nanofiltration and Reverse osmosis have been employed to remove heavy metal contaminants from water. Tables 11 and 12 show a summary of the types of membrane filtration, applications and advantages.

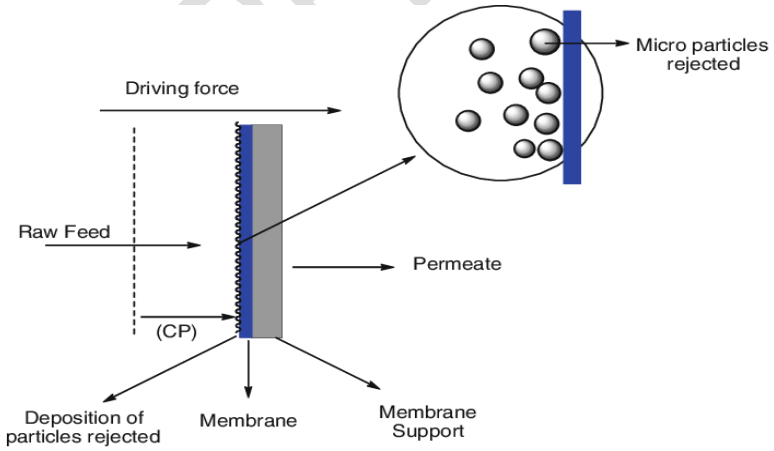


Figure 5: Schematic of Membrane filtration [74]

Table 11: Types of Membrane Filtration

Type	Characteristics	Component Material	Reference

Microfiltration	Pore size: 0.03 to 10 microns Operating Pressure: 100 to 400 kPa (15 to 60psi) MWCO >100,000 Da	natural or synthetic polymers(polyamides, polysulfide, polypropylene, and polytetrafluoroethylene (PTFE)) Ceramic, glass and zirconium oxide	[73], [75]
UltraFiltration	Pore Size: 0.002 to 0.1 microns Operating Pressure: 200 to 700 kPa (30 to 100 psi) MWCO 10,000 to 100,000Da	Polymers (polysulfone, polypropylene, nylon 6, PTFE, polyvinyl chloride, and acrylic copolymer). Ceramics, carbon-based membranes, and zirconia.	[76]
Nano Filtration	Pore Size: 0.001 microns Operating pressure: 600 to1,000 kPa (90-150psi) MWCO 1,000 to 100,000Da	cellulose acetate and aromatic polyamide	[72] [73]
Reverse Osmosis	Operating Pressure:1000 to 10,000kPa(145-1450psi)	Polymers(polyamines and polyureas), cellulosic acetate and matic polyamide	[75] [73]

*MWCO= Molecular Weight Cut-Off ; *Da= Daltons

Table 12: Applications of Membrane Filtration

Type	Applications	Advantages	Disadvantages
Micro Filtration	Used to disinfect water solutions. Sterile filtration of parental fluids. Sterile filtration of air. Preparation of particulate, ultra-pure water for the electronics industry Treatment of municipal sewage Oil emulsion waste treatment	Bacterium with a diameter of 0.3 μm can be disinfected by a MF membrane.	Organic and inorganic substances are able to pass through MF membranes
Ultra Filtration	Production of ultra-pure water for electronics industry Reduction of high COD levels in corn starch plants Selective removal of dissolved toxic metals from groundwater in combination with chemical treatment Treatment of whey in dairy industries Wine or fruit juice clarification	Simple Automation. No need for chemicals (coagulants, flocculants, disinfectants, pH adjustment)	High Membrane fouling
Nano Filtration	Used in environment-friendly and energy-efficient applications like ground water, surface water, and wastewater treatment purposes.	Effectively removes hardness of water thereby eliminating use of chemical softeners. Simplification of cleaning-up processes of wastewaters.	Membranes also remove alkalinity which makes product water corrosive.

Reverse Osmosis	Boiler feed water and cooling tower blow down recycle for utilities and power generation Cleaning of contaminated surface water and groundwater Potable water from sea or brackish water Pharmaceutical-grade water Ultra-pure water for food processing and electronic industries Water for chemical, pulp, and paper industry	Easy reuse of sludges and decrease of disposal costs Removes nearly all contaminant ions and most dissolved non-ions. Bacteria and particles are also removed Operates without any minimum break-in period No latent heat of vaporization or fusion is required for effecting separations	High capital and operating costs High level of pretreatment is required in some cases. Membranes are prone to fouling

Source: [73]

Nano Filtration: Its separation mechanism involves steric (sieving) and electrical (Donnan) effects [77]. A Donnan potential is created between the charged anions in the NF membrane and the cations in the effluent. The significance of this membrane lies in its small pore and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts [77]. [78] performed a comparative analysis using two nanofiltration membranes for the removal of Zn, Cu, and Cd from Industrial wastewater of a Tunisian wiring industry. Both membranes showed a removal efficiency of between 62-93% removals of the selected heavy metals confirming that nano filtration is an effective method for heavy metal rejection.

Reverse osmosis (RO): This is a pressure-driven membrane process that allows water to pass through the membrane, while the heavy metal is retained [77]. Operational simplicity and automation allow for less operator attention and make the process suitable for small system applications Separation of non metallic components can also be achieved using Membrane filtration. [79] applied membrane filtration for the removal of ammonium ions from potable water resulting in 96% filtration using Reverse osmosis.

Hybrid methods of combining two or more separation techniques to improve filtration have also been evaluated. These methods combine advantages of the processes to further improve efficiency of removal. [80] utilized flotation (using synthetic zeolite as binding agent) and microfiltration to remove copper, nickel and zinc from wastewater. Flotation forces the collision of the pollutants which results in formation of high concentration that can readily be eliminated through membrane filtration. This also involves separating the loaded bonding agents from the wastewater stream by separation processes and eventually regenerating the bonding agent, making water as well as metal reuse possible [80]. The experiment analysis indicated that the metals namely copper, nickel and zinc, were reduced from initial concentrations of 474, 3.3 and 167 mg/L , respectively, to below 0.05 mg/L with corresponding removal

efficiency of >99.99% for copper, >99.97% for zinc and >98.5% for nickel. Figure 6 shows the flow scheme of the hybrid process lab-scale plant used for the investigation

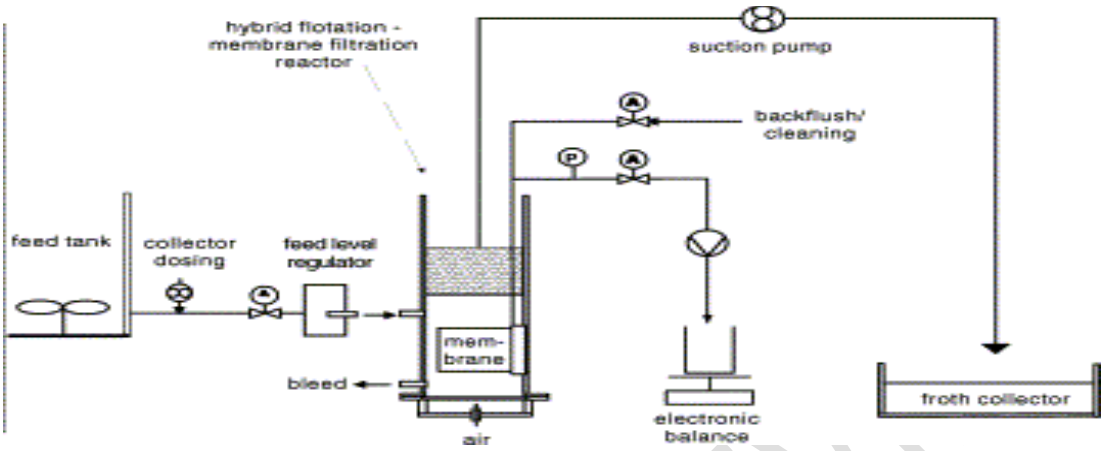


Figure 6: Flow scheme of the hybrid process lab-scale plant used for the investigation [80]

Results from various studies using various membrane filtration techniques are listed in Table 13.

Table 13: Percent (%) Removal of Heavy Metals using Membrane Filtration

Metal	Initial Conc(mg/L)	Application	Pressure (Bar)	Optimum pH	% Removal	Reference
Cu(II)	474	Hybrid MF	0.015	8	99.99	[80]
Zn(II)	167	Hybrid MF	0.015	8	99.97	[80]
Ni(II)	3.3	Hybrid MF	0.015	8	98.5	[80]
Pb(II)	10	UF	0.69	7	99.3	[81]
Cd(II)	7	UF	0.69	7	83.4	[81]
Zn(II)	10	UF	5	8	83	[82]
Ni(II)	10	UF	5	8	93	[82]
Al(II)	134	UF	5	3	24	[83]
Ni(II)	5.3	UF	5	3	34	[83]
Cr(II)	1.3	UF	5	3	46	[83]
Al(II)	64.9	NF	10	3	91	[83]
Ni(II)	4.6	NF	10	3	97	[83]
Cr(II)	0.2	NF	10	3	66	[83]
Al(II)	116.4	NF	15	3	98	[83]
Ni(II)	4.6	NF	15	3	99	[83]
Cr(II)	0.2	NF	15	3	89	[83]
Al(II)	129.3	NF	20	3	99	[83]
Ni(II)	5.3	NF	20	3	99	[83]
Cr(II)	0.6	NF	20	3	94	[83]
Al(II)	134.6	RO	10	3	99	[83]
Ni(II)	5.0	RO	10	3	99	[83]
Cr(II)	1.3	RO	10	3	97	[83]

Al(II)	100.8	RO	20	3	99	[83]
Ni(II)	3.8	RO	20	3	99	[83]
Cr(II)	0.35	RO	20	3	94	[83]
Zn(II)	10 mol/L	NF	4	NA	76	[78]
Cu(II)	10 mol/L	NF	4	NA	95	[78]
Cd(II)	10 mol/L	NF	4	NA	62	[78]

*NA= Not Available NF= NanoFiltration RO= Reverse Osmosis UF= Ultra Filtration MF= Micro Filtration

However, membrane filtration suffers from high manufacturing costs and low tolerance to high pressure/temperature. Oxidation process generally involves the use of UV and/or strong oxidants, and the operating procedures are complex and costly for large scale utilizations.

6. ELECTRODIALYSIS

Electrodialysis is a membrane separation process in which ions are transported through ion selective membranes from one solution to another under the influence of an electric field [30].The use of electrodialysis is particularly significant because it approaches membrane technology as an advanced environmental technology that enables the development of clean treatment sequences for the recovery of water in industrial processes [30]. This treatment method has been applied for remediation of heavy metal polluted soils, industrial effluents and more recently stirred suspensions [84].The operation of Electrodialysis is driven by the development of ion exchange membrane that produces high water recovery and does not require phase change, reaction, or chemicals. These advantages provide environmental benefits without the use of fossil fuels and chemical detergents [85]. A cell consists of a volume with two adjacent membranes. If an ionic solution such as an aqueous salt solution is pumped through these cells and an electrical potential is established between the anode and cathode, the positively charged cations migrate towards the cathode and the negatively charged anions towards the anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion-exchange membrane. Likewise, the negatively charged anions pass through the anion-exchange membrane, and are retained by the cation exchange membrane. The overall result is an increase in the ion concentration in alternate compartments, while the other compartments simultaneously become depleted. The depleted solution is generally referred to as the diluate and the concentrated solution as the brine or the concentrate. The driving force for the ion transport in the electrodialysis process is the applied electrical potential between the anode and cathode[86]. A schematic of the process is shown in Figure 7.

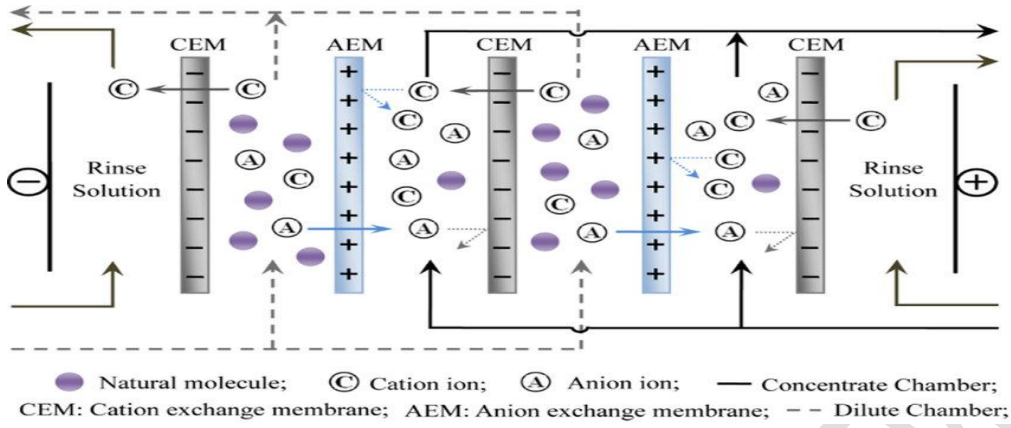


Figure 7: Schematic of Electrodialysis process [87]

The controlling parameters for an electrodialysis system include Electrical conductivity, pH, concentration of ions, electric current/applied potential and limiting current density [30]. This process is used to treat wastewater from industrial effluents (metal finishing, tanning, pulp and paper processing), municipal or animal farming sources contain heavy metal ions and acids as well as nutrients. Properties such as selectivity, high separation efficiency, and chemical-free treatment make Electrodialysis methods adequate for desalination and other treatments with significant environmental benefits [88]. Results obtained from some research works using this process to remove heavy metals from wastewater are shown in Table 14. One major limitation of in the use of electrodialysis in wastewater treatment is that the process removes only ions leaving behind bacteria and other organic contaminants in the treated water making it unsuitable for household use. Other limitations include high operational costs and relatively high energy requirement for water treatment. This method is therefore optimally used to treat brackish water for industrial purposes [89].

Table 14: Electrodialysis treatment of wastewater

Metal	Initial Conc(mg/L)	Electrode	Contact time (Hours)	Removal (%)	Current Density (mA/cm^2)	References
Cd(II)	163ug/L	C-Fe	8	74.8	3A	[90]
Sn(II)	122ug/L	C-Fe	8	64.5	3A	[90]
Cr(III)	570	Al-Fe	45 minutes	100	14	[91]
Cu(II)	100	C-Fe	75 minutes	99.9	NA	[92]
Cu(II)	209.1	Pt	5	95	5.9	[93]
Ni(II)	82.7	Pt	2	95	5.9	[93]
Cd(II)	2,000	Pt	2	21.4	15	[94]

Fe(III)	82	Pt-Fe	3	16	10	[95]
Cu(II)	244.3	Pt-Fe	3	49.8	10	[95]
Ni(II)	1247.7	Pt-Fe	3	40.5	10	[95]
Al(III)	251.2	Pt-Fe	3	67.7	10	[95]
Cr(VI)	100	NA	75 minutes	99	0.03A	[96]
Cr(VI)	480	C-Fe	24	70.5	3A	[90]

7. PHOTOCATALYSIS

The possibility to utilize solar energy as a free energy from nature to solve the environmental problems is the key significance of photocatalysis [97]. Photocatalysis is a type of reaction that occurs when a chemical reaction is accelerated in the presence of a catalyst on exposure to light (photon (hv)). There are 2 types of photocatalytic reactions, Homogeneous Photocatalysis which takes place when the catalyst is in the same phase with the reactant and Heterogeneous Photocatalysis which takes place when the catalyst is in a different phase (mostly solid) with the reactant.

In Heterogeneous photocatalysis, metal oxides (semi conductors) are used in the form of suspended phase or immobilized state. Some of the metal oxides used are titanium (TiO_2), zinc (ZnS and ZnO), tungsten, vanadium, Tin (SnO_2) and chromium. Figure 8 shows the historic development of photocatalysts used from 1960 to present day. The illumination of light over the heterogeneous photocatalyst by photons with energy at least equal to its band gap energy can generate the electron–hole pairs. The photo-activated electrons are transferred from the valence band to the conduction band, leaving the positive holes in the valence band. Subsequently, the photo-activated electrons and holes can migrate from bulk to the surface of photocatalyst and react with some adsorbed substances on the surface to generate the free radicals [97]. Titanium dioxide (TiO_2) is by far the most useful SC material for photocatalytic purposes because of its exceptional optical and electronic properties, chemical stability, nontoxicity, and low cost [98]. A schematic of the phtocatalytic process is shown in Figure 9.

When a solution containing pollutants is introduced into a photocatalytic system, a four step process is conducted. The pollutants transfer to the surface from the aqueous phase. They are then absorbed by the semiconductor surface. The next step is photocatalytic reactions occurring

in the absorbed phase. The products are then decomposed and removed from the interface region [72].

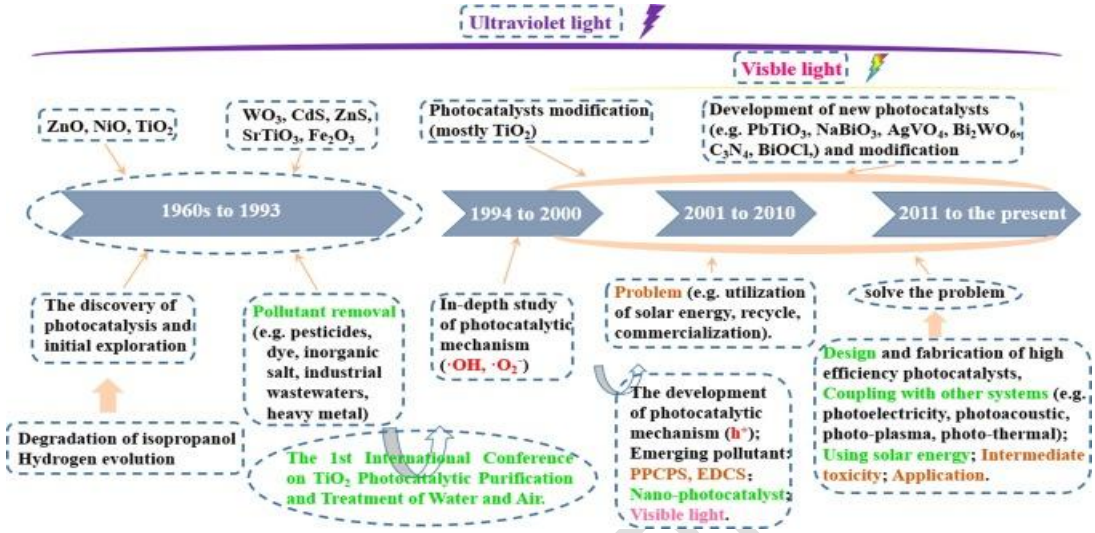


Figure 8: Historic development of Photocatalysts [99]

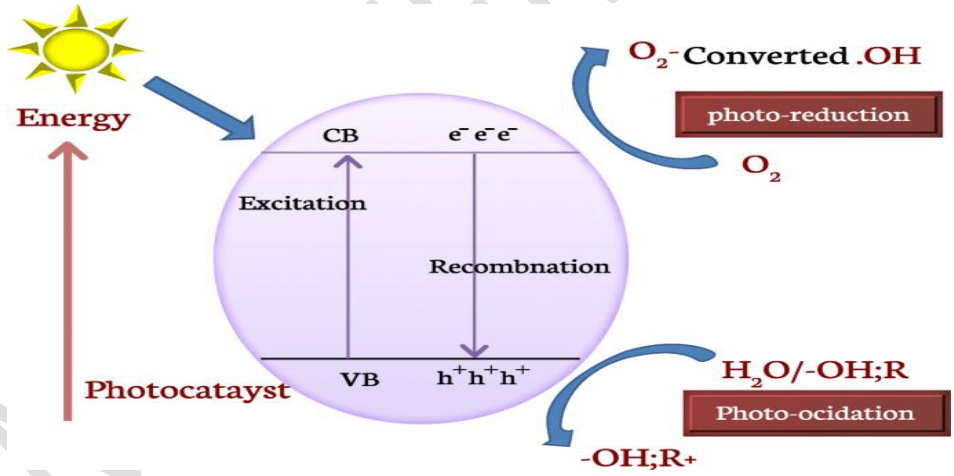


Figure 9: Schematic of Photocatalytic Process [100]

The process gradually breaks down the contaminant molecule so that no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required. This result in considerable savings and a simpler operation of the equipment involved [101]. Photocatalytic process is used for a wide range of water treatment processes including treatment of brackish

water, water disinfections, degradation of natural organic matter and destruction of organics (Aromatic Hydrocarbons). These advantages mean that the process results in considerable savings in the water production cost and keeping the environment clean.

[102] studied the use of Bi_2WO_6/mesoporous TiO_2 nanotube composites (BWO/TNTs) to remove the heavy metal Cr (VI) and refractory organic compound dibutyl phthalate (DBP) from contaminated water under visible light. It was noted that the composite was able to degrade the Cr(VI) to a more non toxic Cr(III).

[103] studied the use of hybrid MoSe2/BiVO4 photocatalyst to remove of Cu, Cd, Pb, Cr and Zn with initial concentrations 2.159, 0.227, 0.257, 0.723 and 0.143mg/L from industrial waste water. The optimum experimental conditions were observed at pH of 9, 0.5mg CuCo2S4 as catalyst at a time of 210 minutes for 99.9% removal of the heavy metals from the water sample.

The use of a chitosan/Ag bionanocomposites as eco-friendly photocatalytic reactor was studied by [104]. The reaction rates and percentage removal for Cd, Pb and Cu were studied and results showed reaction rates of $1.5 *10^{-4}$ mol dm^{-3} s^{-1}, $1.4 *10^{-4}$ mol dm^{-3} s^{-1} , $1.1*10^{-4}$ mol dm^{-3} s^{-1} and percentage removal of 89%, 88% and 97% for Cd,Pb and Cu respectively.

[105] studied the simultaneous removal of Cr(VI) and phenol from water using Titanium Dioxide(TiO_2) Photocatalyst. The study showed a removal efficiency of 67.2% of Cr(VI) in the presence of phenol at initial concentration of 100mg/ml and pH of 7.

[106] studied the removal of Heavy metals from Pharmaceutical Waste water using a ZnO Nano Composite Semiconductor as photocatalyst. The research observed the reduction of Cu, Cr, Pb, Ni, Zn and Cd from initial concentrations of 1.158, 0.415, 0.247, 0.145, 0.131 and 0.127mg/Kg respectively to 0.421, 0.211, 0.147, 0, 0 and 0.097 mg/Kg respectively. This result shows that the ZnO Nano composite catalyst was able to completely eliminate Nickel and Zinc pollutants from the effluent.

A major disadvantage of photocatalysis process is that industrial wastewaters usually contain several organic and inorganic pollutants which compete for the adsorption sites of the semi conductor surface, thus inhibiting the efficiency of the process for removal of heavy metals

[107]. The exception being Cr(VI) which shows better removal efficiency in the presence of organic impurities [108].

8. HYBRID TREATMENT TECHNIQUES

Hybrid treatment methods are being adopted to tackle industrial effluents due to the diversities of pollutants found in their waste water. More Industries now have diverse production activities which infuse diverse pollutants into the waste water. These new generation of micropollutants and bioactive compounds associated with polluted water needs sustainable systems with low energy consumption [109]. Conventional methods of treatment may be ineffective to deal with these new pollutants hence the need to introduce hybrid treatment methods that utilize a combination of two or more of these processes. There is also the issue of large energy consumption associated with convectional waste water treatment processes which has necessitated the research of more energy efficient processes. High energy consumption not only increases cost of operation but also affects the environment negatively. Some of these include Photo-Fenton process, Fenton, advanced oxidation and hydrodynamic cavitation processes. While research into the use of these processes is still ongoing, there have been successes in the use of some of these methods in the treatment of some industrial effluents. Hydrodynamic cavitation process has been used for the extraction of cobalt (II) from wastewater [110] and reduction of Cu (II), Fe(III), Ni(II) and Mn(II) contamination by 70.8%, 95.3%, 94.54% and 46.8% respectively from industrial waste water [111]. More research into the removal of heavy metals using these hybrid techniques are still ongoing and are the future of water treatment.

9. CONCLUSION

Review of different methods of water treatment showed that while each treatment method has inherent advantages and some disadvantages based on efficiency of removal and cost of operation. In chemical precipitation method, it has been found as an effective method for heavy metal decontamination of water, a major disadvantage of the process is the formation of a large quantity of metal precipitate which requires further treatment and disposal. Membrane filtration suffers from high

manufacturing costs and low tolerance to high pressure/temperature. Oxidation process generally involves the use of UV and/or strong oxidants, and the operating procedures are complex and costly for large scale utilizations. One major limitation of in the use of electrodialysis in wastewater treatment is that the process removes only ions leaving behind bacteria and other organic contaminants in the treated water making it unsuitable for household use. Other limitations include high operational costs and relatively high energy requirement for water treatment. This method is therefore optimally used to treat brackish water for industrial purposes Photocatalytic process is used for a wide range of water treatment processes including treatment of brackish water, water disinfections, degradation of natural organic matter and destruction of organics (Aromatic Hydrocarbons). These advantages mean that the process results in considerable savings in the water production cost and keeping the environment clean. A major disadvantage of photocatalysis process is that industrial wastewaters usually contain several organic and inorganic pollutants which compete for the adsorption sites of the semi conductor surface, thus inhibiting the efficiency of the process for removal of heavy metals . The exception being Cr(VI) which shows better removal efficiency in the presence of organic impurities. Other methods are also found to remove nearly 100% of heavy metals when used as a hybrid operation of 2 or more methods.

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